

104-088737

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JC13 Rec'd PCT/PTO 22 MAR 2002

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March 22, 2002

**BOX PCT**

Commissioner for Patents  
Washington, D.C. 20231

PCT/AU00/01180  
-filed September 22, 2000

Re: Application of Albert MAU, Li-ming DAI and Shaoming HUANG  
PATTERNED CARBON NANOTUBES  
**Assignee: COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH  
ORGANISATION**  
Our Ref: Q69176

Dear Sir:

The following fee is submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty:

The Declaration and Power of Attorney, Assignment, will be submitted at a later date.

It is assumed that copies of the International Application, the International Search Report, the International Preliminary Examination Report, and any Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

The Government filing fee is calculated as follows:

|                    |           |   |    |   |           |   |         |   |                 |
|--------------------|-----------|---|----|---|-----------|---|---------|---|-----------------|
| Total claims       | <u>43</u> | - | 20 | = | <u>23</u> | x | \$18.00 | = | <u>\$414.00</u> |
| Independent claims | <u>1</u>  | - | 3  | = |           | x | \$84.00 | = | <u>\$ .00</u>   |
| Base Fee           |           |   |    |   |           |   |         |   | <u>\$890.00</u> |

**TOTAL FEE**

\$1304.00

A check for the statutory filing fee of \$1304.00 is attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from:

Country

Application No


Filing Date

Australia

PQ 3041

September 23, 1999

Respectfully submitted,

  
Robert V. Sloan  
Registration No. 22,775

RVS/amt

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Docket No: Q69176

Albert MAU, et al.

Appln. No.: 10/088,737

Group Art Unit: Not Yet Assigned

Confirmation No.: 4585

Examiner: Not Yet Assigned

Filed: March 22, 2002

For: PATTERNED CARBON NANOTUBES

**PRELIMINARY AMENDMENT**

Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-identified application as follows:

**IN THE SPECIFICATION:**

**Please amend the specification as follows:**

Page 1, before the first full paragraph insert the heading

**BACKGROUND OF THE INVENTION**

after the first full paragraph insert the heading

**SUMMARY OF THE INVENTION**

Page 8, delete the heading "Referring to the drawings:" and insert the heading

**BRIEF DESCRIPTION OF THE DRAWINGS**

Page 9, delete the heading "EXAMPLES" and insert the heading

**DETAILED DESCRIPTION OF THE INVENTION**

PRELIMINARY AMENDMENT  
USSN: 10/088,737

**IN THE CLAIMS:**

Delete the heading THE CLAIMS: and insert the heading

**WHAT IS CLAIMED IS:**

**IN THE ABSTRACT:**

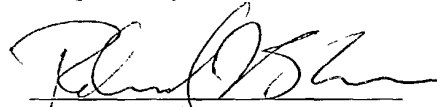
Please delete the present Abstract of the Disclosure and replace it with the following  
substitute Abstract found on the attached unnumbered sheet.

PRELIMINARY AMENDMENT  
USSN: 10/088,737

**REMARKS**

The application has been amended to provide appropriate headings for the various sections of the specification and to place the Abstract into proper one paragraph format. Entry and consideration of this Amendment and an early and favorable action on the merits is respectfully requested.

Respectfully submitted,



Robert V. Sloan  
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Date: June 19, 2002

PRELIMINARY AMENDMENT  
USSN: 10/088,737

**APPENDIX**

**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE SPECIFICATION:**

**Please amend the specification as follows:**

Page 1, before the first full paragraph insert the heading

**BACKGROUND OF THE INVENTION**

after the first full paragraph insert the heading

**SUMMARY OF THE INVENTION**

Page 8, delete the heading “Referring to the drawings:” and insert the heading

**BRIEF DESCRIPTION OF THE DRAWINGS**

Page 9, delete the heading “EXAMPLES” and insert the heading

**DETAILED DESCRIPTION OF THE INVENTION**

**IN THE CLAIMS:**

Delete the heading THE CLAIMS: and insert the heading

**WHAT IS CLAIMED IS:**

**IN THE ABSTRACT:**

**Please delete the present Abstract of the Disclosure and replace it with the following  
substitute Abstract found on the attached unnumbered sheet.**

## ABSTRACT

--A process for preparing a patterned layer of aligned carbon nanotubes on a substrate including: applying a pattern of polymeric material to the surface of a substrate capable of supporting nanotube growth using a soft-lithographic technique; subjecting said polymeric material to carbonization to form a patterned layer of carbonized polymer on the surface of the substrate; synthesising a layer of aligned carbon nanotubes on regions of said substrate to which carbonized polymer is not attached to provide a patterned layer of aligned carbon nanotubes on said substrate.--

10/088737  
13 Rec'd PCT/PTO 19 JUN 2002  
10/088737

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Docket No: Q69176

Albert MAU, et al.

Appln. No.: 10/088,737

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For: PATTERNED CARBON NANOTUBES

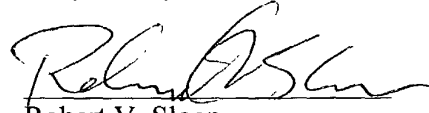
**SUBMISSION OF FORMAL DRAWINGS**

Commissioner for Patents  
Washington, D.C. 20231

Sir:

Submitted herewith please find 6 sheets of formal drawings. The Examiner is respectfully requested to acknowledge receipt of these formal drawings.

Respectfully submitted,



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Date: June 19, 2002

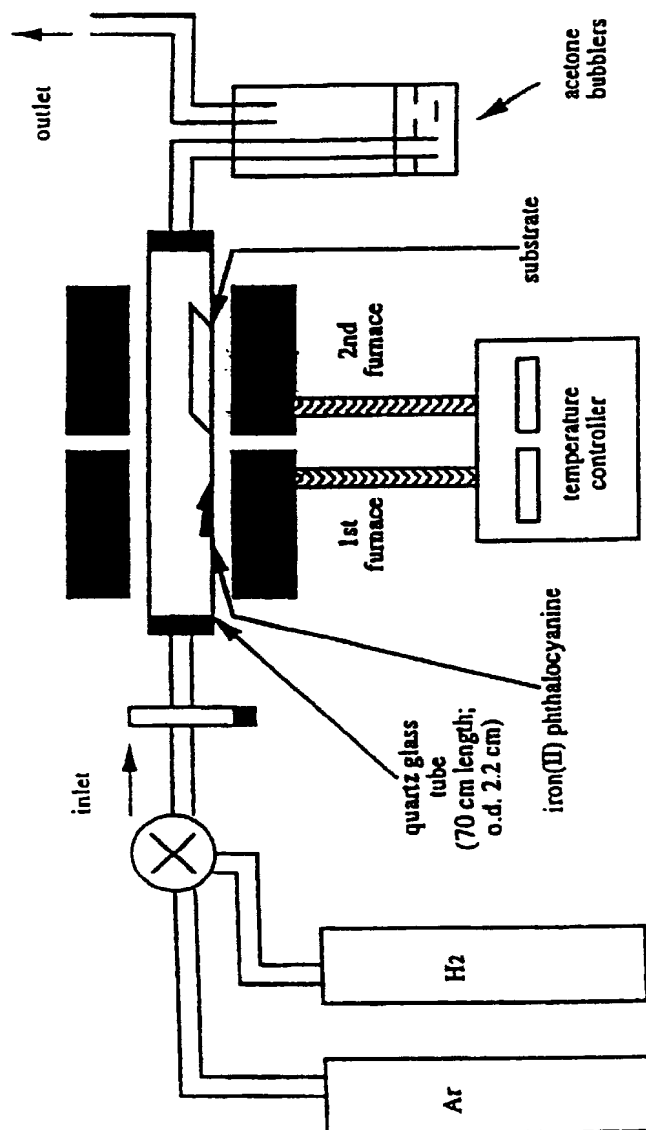


FIGURE 1



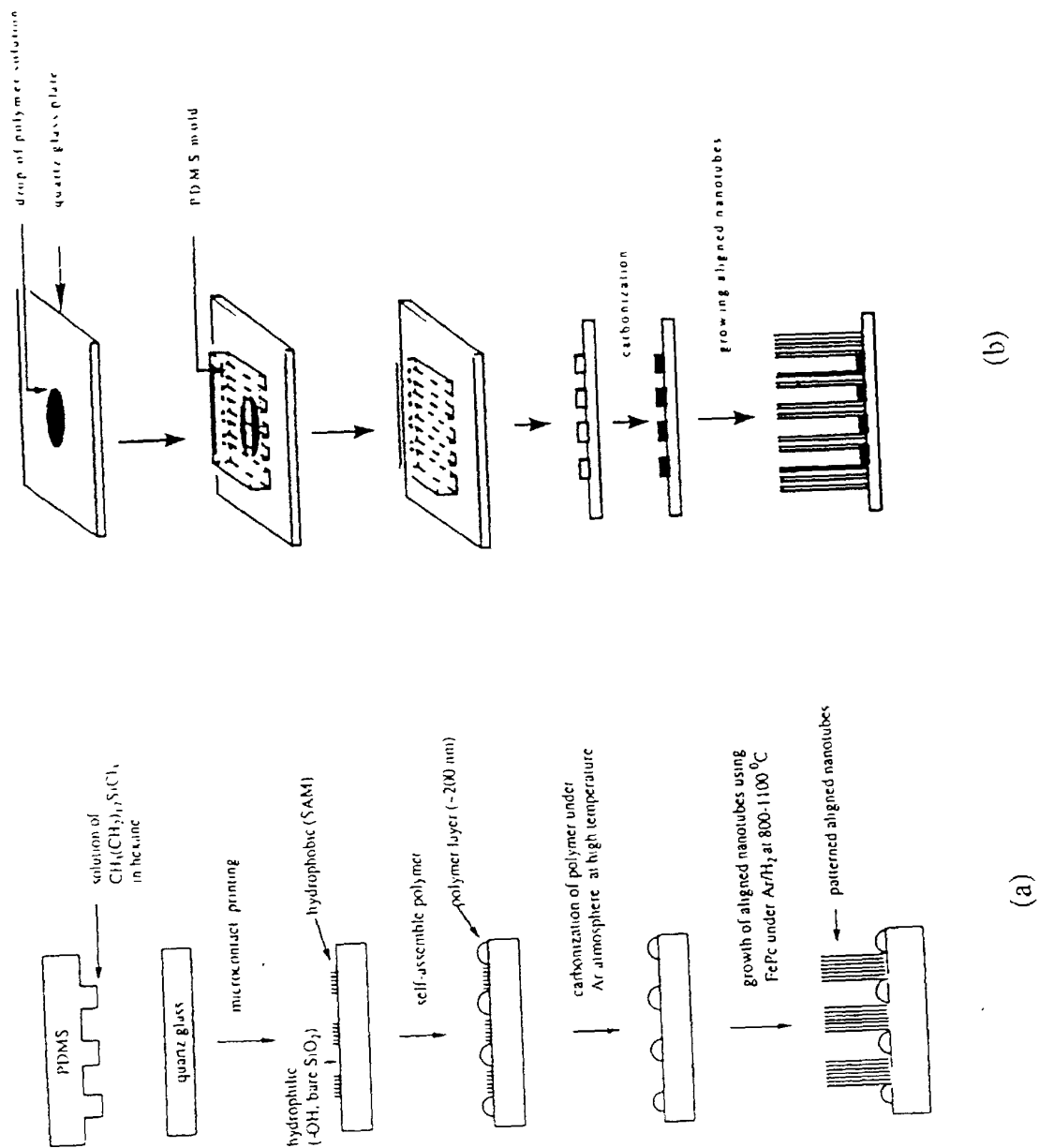


FIGURE 2

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Figure 3(a)

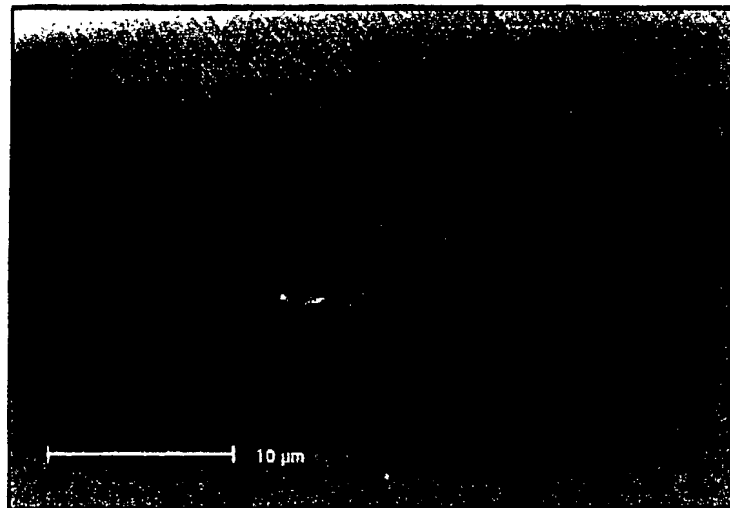


Figure 3(b)

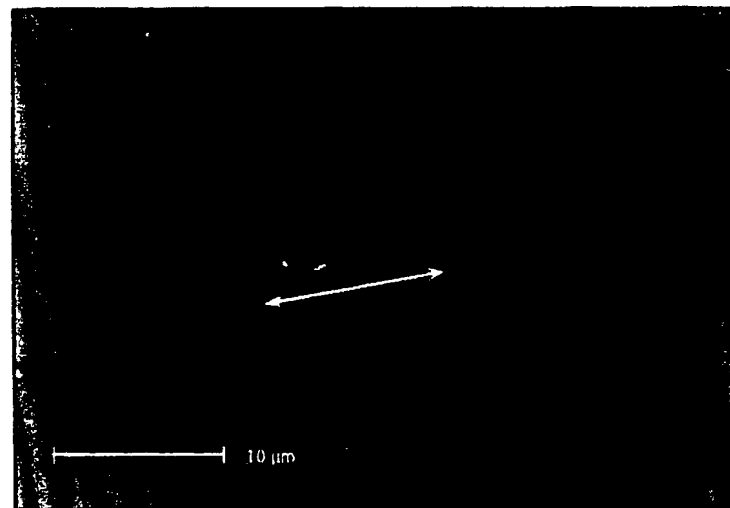


Figure 3(c)

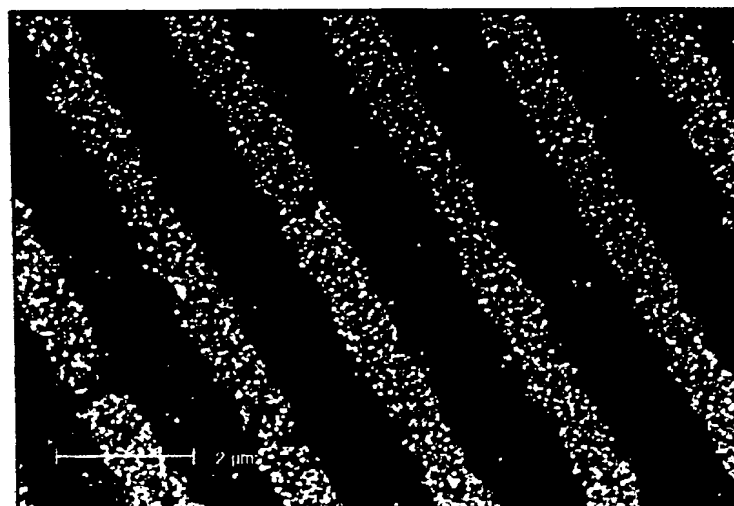


Figure 3(d)

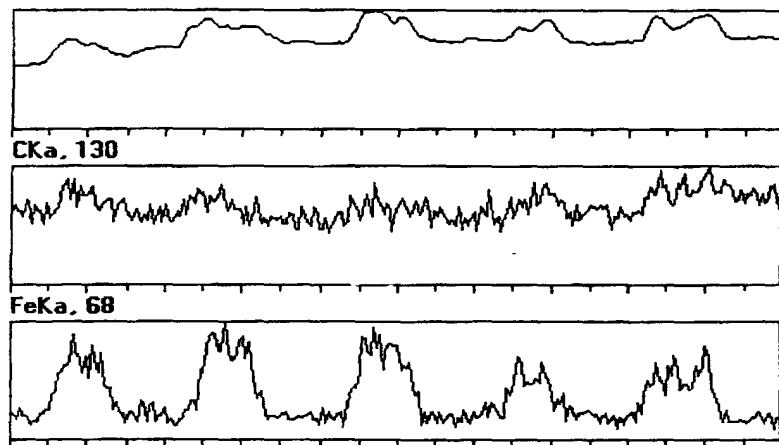


Figure 3(e)

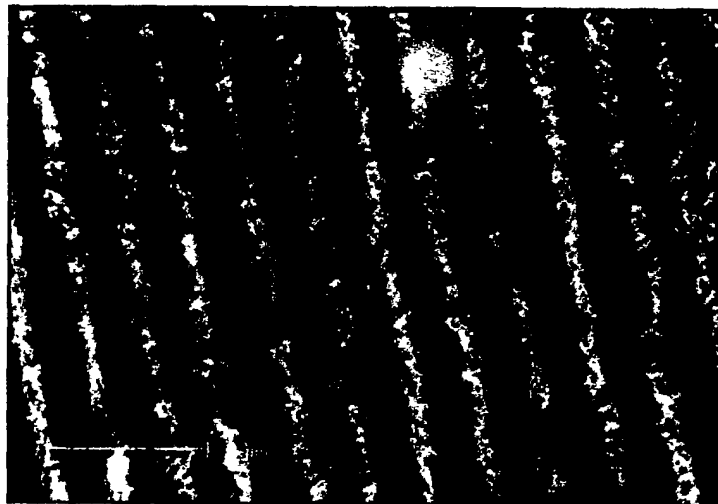


Figure 3(f)

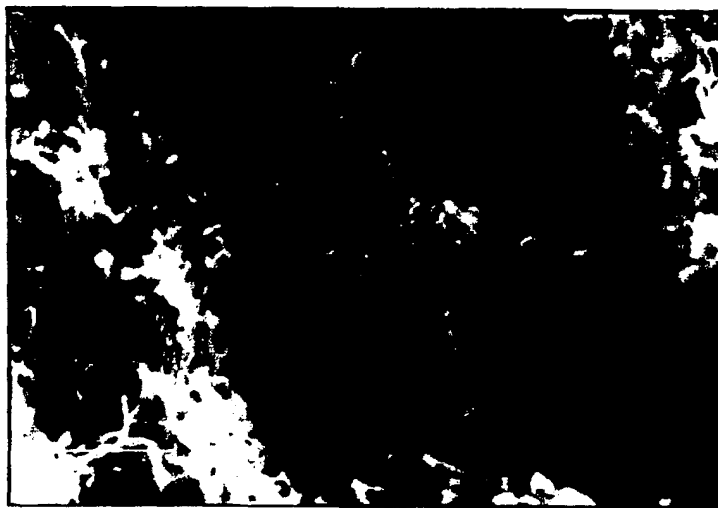


Figure 4(a)

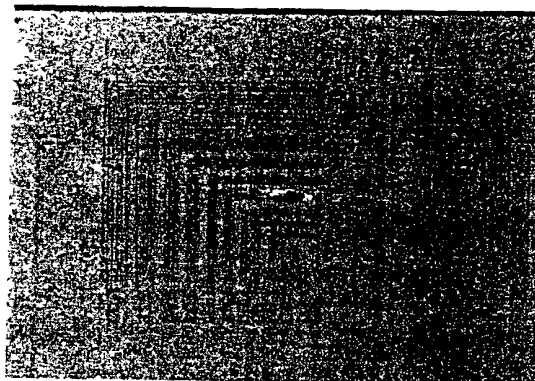


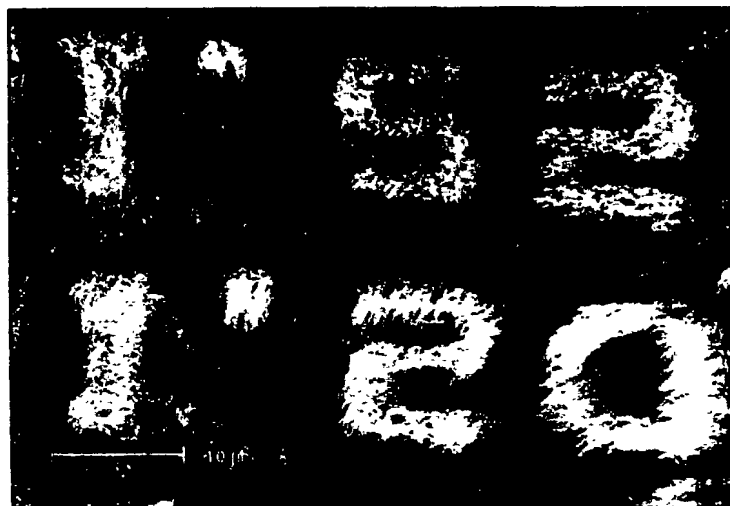
Figure 4(b)



Figure 4(c)



Figure 4(d)



## PATTERNED CARBON NANOTUBES

This invention relates to carbon nanotube materials and processes for their preparation. In particular the invention relates to patterned aligned carbon nanotubes and to processes for  
5 their preparation which involve the use of a soft-lithographic technique. The invention also relates to the construction of various electronic and photonic devices from such materials for practical applications in many area including as electron field emitters, artificial actuators, chemical sensors, gas storages, molecular filtration membranes, energy absorbing materials, molecular transistors and other opto electronic devices.

10

Soft-lithography has recently become a very promising technique for micro-/nano-structuring a wide range of materials (see, for example: Xia, Y.; Whitesides, G.M. *Annu. Rev. Mater. Sci.* **1988**, 28, 153). Various strategies, including micro-contact printing ( $\mu$ CP), mechanical scraping, and micro-molding, have been developed for nanoscale patterning that otherwise  
15 is difficult by photolithographic techniques (see, for example: Dai, L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1999**, 39, 273, and references cited therein). In particular, micro-contact printing ( $\mu$ CP) has been demonstrated to be a very convenient patterning technique for generating self-assembled monolayer (SAM) patterns of certain molecular "inks" (e.g. alkanethiol, alkylsiloxane) on an appropriate substrate surface (e.g. gold, silver, copper,  
20 aluminium, and silicon dioxide surfaces) using an elastomeric stamp (typically, a polydimethylsiloxane (PDMS) stamp) for a region-specific transfer of the SAM material. On the other hand, the solvent-assisted micromolding (SAMIM) technique allows pattern formation through confined solvent evaporation from a thin layer of polymer solution sandwiched between a PDMS elastomer mold and substrate surface. However, it has been  
25 a major challenge for researchers to find ways to control the arrangement of carbon nanotubes.

Carbon nanotubes usually have a diameter in the order of tens of angstroms and the length of up to several micrometers. These elongated nanotubes consist of carbon hexagons arranged  
30 in a concentric manner with both ends of the tubes normally capped by pentagon-containing, fullerene-like structures. They can behave as a semiconductor or metal depending on their

diameter and helicity of the arrangement of graphitic rings in the walls, and dissimilar carbon nanotubes may be joined together allowing the formation of molecular wires with interesting electrical, magnetic, nonlinear optical, thermal and mechanical properties. These unusual properties have led to diverse potential applications for carbon nanotubes in material science and nanotechnology. Indeed, carbon nanotubes have been proposed as new materials for electron field emitters in panel displays, single-molecular transistors, scanning probe microscope tips, gas and electrochemical energy storages, catalyst and proteins/DNA supports, molecular-filtration membranes, and energy-absorbing materials (see, for example: M. Dresselhaus, *et al.*, *Phys. World*, January, 33, 1998; P.M. Ajayan, and T.W. Ebbesen, *Rep. Prog. Phys.*, 60, 1027, 1997; R. Dagani, *C&E News*, January 11, 31, 1999).

For most of the above applications, it is highly desirable to prepare aligned carbon nanotubes so that the properties of individual nanotubes can be easily assessed and they can be incorporated effectively into devices. Carbon nanotubes synthesised by most of the common techniques, such as arc discharge, often exist in a randomly entangled state. However, aligned carbon nanotubes have recently been prepared either by post-synthesis manipulation or by synthesis-induced alignment (see, for example: S. Huang, L. Dai and A.W.H. Mau, *J. Mater. Chem.* (1999), 9, 1221 and references cited therein).

The number of techniques which have been reported for the pattern formation of aligned carbon nanotubes is very limited (S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell, and H. Dai, *Science*, 283, 512, 1999; S. Huang, L. Dai, and A.W.H. Mau, *J. Phys. Chem.*, 103 issue 21, 4223-4227), and the achievable resolutions of the nanotube patterns was, at the best, at several micrometer scale in these cases.

It has now been found that pattern formation of perpendicularly aligned carbon nanotubes with resolutions up to a sub-micrometer scale can be achieved using a novel soft-lithographic technique.

According to a first aspect, the present invention provides a process for preparing a patterned layer of aligned carbon nanotubes on a substrate including:

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applying a pattern of polymeric material to the surface of a substrate capable of supporting nanotube growth using a soft-lithographic technique,

5       subjecting said polymeric material to carbonization to form a patterned layer of carbonized polymer on the surface of the substrate,

10       synthesising a layer of aligned carbon nanotubes on regions of said substrate to which carbonised polymer is not attached to provide a patterned layer of aligned carbon nanotubes on said substrate.

The polymeric material may be any polymer capable of being applied to the substrate surface in the form of a pattern using a soft-lithographic technique, and which is capable of undergoing carbonization. The pattern of carbonized polymer so formed should correspond to the pattern of polymer applied to the substrate using the soft-lithographic technique.

15       Examples of suitable polymers include, but are not limited to, photoresist or photoresponsive materials, such as diazonaphthoquinone (DNQ)-based photo resists (e.g. cresol novolak resin from Shipley, Ozatec PK 14 from Hoechst), as well as other possible polymers including, *inter alia*, epoxy resins, PEO, polyanilines, polymethyl methacrylate, polystyrenes, polydienes and plasma polymers derived from saturated or unsaturated alcohols, ketones,

20       aldehydes, amines or amides. Preferably the polymer is a diazonaphthaquinone (DNQ)-modified cresol novolak photoresist.

The substrate to which the polymer patterned layer is applied can be any substrate which is capable of withstanding the pyrolysis conditions employed, and capable of supporting aligned

25       carbon nanotube growth. Examples of suitable substrates include all types of glass that provide sufficient thermal stability according to the synthesis temperature applied, such as quartz glass, as well as alumina, graphite, mica, mesoporous silica, silicon wafer, nanoporous alumina or ceramic plates. Preferably the substrate is glass, in particular, quartz glass or silicon wafer. The substrate may also include a coating of a material which is capable of

30       supporting carbon nanotube growth under the conditions employed. The coating may be of any metal, metal oxide, metal alloy or compound thereof, which may have conducting or



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semiconducting properties. Examples of suitable metals include Au, Pt, Cu, Cr, Ni, Fe, Co and Pd. Examples of suitable compounds are metaloxides, metal carbides, metal nitrides, metal sulfides and metal borides. Examples of suitable metal oxides include indium tin oxide (ITO),  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{MgO}$ . Examples of semiconducting materials include gallium  
5 arsenide, aluminium arsenide, aluminium sulphide and gallium sulphide.

The patterning of the aligned carbon nanotubes is achieved by creating a region on the substrate which is incapable of supporting nanotube growth. The pattern is created on the substrate using an appropriate soft-lithographic technique. Examples of suitable soft-  
10 lithographic techniques include micro-contact printing ( $\mu\text{CP}$ ) and micro-molding.

In one embodiment the micro-contact printing process involves the region-specific transfer of self-assembling monolayers (SAMs) of a molecular "ink", such as alkylsiloxane, onto a suitable substrate, followed by subsequent adsorption of the polymer in the SAM-free regions.  
15 The transfer of the self-assembling monolayer may be achieved using an appropriate stamp, such as a polydimethylsiloxane (PDMS) stamp. Other processes which involve region-specific transfer of a material which alters the hydrophobicity or hydrophilicity of the substrate surface may also be used, provided the transfer allows subsequent adsorption of the polymer in the more hydrophobic regions of the substrate surface. Using pre-patterned  
20 substrates the polymer patterns may also be prepared by a layer by layer adsorption process through, for example, electrostatic attraction or hydrogen bonding interactions. Furthermore, plasma patterning can be used for the same purpose.

Examples of suitable molecular "inks" include alkanethiols, organosilanes, and their  
25 derivatives, polyelectrolytes, H-bonding molecules, etc.

In another embodiment of the invention the pattern is applied to the substrate using a micro-molding technique. This allows the formation of a patterned polymer coating on the substrate through confined solvent evaporation from a thin layer of polymer solution sandwiched  
30 between a mold, such as an elastomeric mold, and the substrate surface. The elastomeric mold may be made of any suitable material, such as PDMS, fluorocarbon or other solvent

- 5 -

resistant elastomers. The mould surface has incised areas corresponding to the pattern desired which provide channels for the "ink".

Once the polymer pattern is applied to the substrate, the patterned substrate is heated to a temperature at or above the temperature at which the polymer decomposes thereby forming a carbonised pattern on the substrate. In some circumstances it is desirable to heat the polymer material at one or more temperatures below the decomposition temperature of the polymer material. Such heating can stabilise the polymer (e.g. by cross-linking etc.) such that the carbonised polymer pattern remains substantially intact during subsequent pyrolysis.

10

The next step in the process involves the synthesis of a layer of aligned carbon nanotubes on the region of the substrate to which the carbonised polymer is not attached. This may be achieved using a suitable technique for the synthesis of perpendicularly aligned carbon nanotubes. Preferably the aligned carbon nanotubes are prepared by pyrolysis of a carbon-containing material in the presence of a suitable catalyst for nanotube formation.

The carbon-containing material may be any compound or substance which includes carbon and which is capable for forming carbon nanotubes when subjected to pyrolysis in the presence of a suitable catalyst. Examples of suitable carbon-containing materials include alkanes, alkenes, alkynes or aromatic hydrocarbons and their derivatives, for example organometallic compounds of transition metals, for example methane, acetylene, benzene, transition metal phthalocyanines, such as Fe(II) phthalocyanine, and metallocenes such as ferrocene and nickel dicyclopentadiene and any other suitable evaporable metal complex.

25 The catalyst may be any compound, element or substance suitable for catalysing the conversion of a carbon-containing material to aligned carbon nanotubes under pyrolytic conditions. The catalyst may be a transition metal, such as Fe, Co, Al, Ni, Mn, Pd, Cr or alloys thereof in any suitable oxidation state.

30 The catalyst may be incorporated into the substrate or may be included in the carbon-containing material. Examples of carbon-containing materials which include a transition metal

catalyst are Fe(II) phthalocyanine, Ni(II) phthalocyanine and ferrocene. When the catalyst and carbon-containing material are included in the same material it may be necessary to provide sources of additional catalyst or additional carbon-containing material. For example, when ferrocene is used as the catalyst and a source of carbon, it is necessary to provide an  
5 additional carbon source, such as ethylene, to obtain the required nanotube growth.

The pyrolysis condition employed will depend on the type of carbon-containing material employed and the type of catalyst, as well as the length and density of the nanotubes required. In this regard it is possible to vary the pyrolysis conditions, such as the temperature, time,  
10 pressure or flow rate through the pyrolysis reactor, to obtain nanotubes having different characteristics.

For example, performing the pyrolysis at a higher temperature may produce nanotubes having different base-end structures relative to those prepared at a lower temperature. The pyrolysis  
15 will generally be performed within a temperature range of 500°C to 1100°C. Similarly lowering the flow rate through a flow-type pyrolysis reactor may result in a smaller packing density of the nanotubes and vice versa. A person skilled in the art would be able to select and control the conditions of pyrolysis to obtain nanotubes having the desired characteristics.

20 After synthesis of the layer of aligned carbon nanotubes in the patterned array on the substrate, the carbonised polymer remaining on the substrate may be dissociated from the carbon nanotubes. This may be achieved by plasma etching. Alternatively it is possible to disassociate the carbon nanotubes from the substrate by transferring the patterned carbon nanotube layer to another substrate. This other substrate may be another substrate capable  
25 of supporting carbon nanotube growth, or may be a metal, metal oxide, semi-conductor material or a polymer. Examples of suitable polymers include adhesive coated polymers such as cellulose tape, conjugated (conducting) polymers, temperature/pressure responsive polymers, bioactive polymers and engineering resins.

30 Where the patterned layer of aligned carbon nanotubes is transferred to another substrate which is capable of supporting carbon nanotube growth, it is possible to form a hetero-

- 7 -

structured nanotube film by subjecting the nanotube coated substrate to conditions for promoting aligned carbon nanotube growth. The conditions of nanotube formation may be controlled or adjusted such that the length of the further nanotubes is different to the length of the nanotubes making up the original patterned layer. This second layer of nanotubes will  
5 tend to grow in the spaces defined by the original patterned layer. It may also be possible to adjust conditions such that there is some further nanotube growth on top of the original patterned layer.

The nanotube patterns on quartz plates may also be separated from the substrate, while  
10 retaining the integrity of the pattern by immersing the sample in an aqueous hydrofluoric acid solution (10-40% w/w) for an appropriate period.

For some applications, the patterned carbon nanotube film may be incorporated into a multilayer structure including layers of other materials, such as metals, metal oxides,  
15 semiconductor materials or polymers.

The patterned carbon nanotube film prepared in accordance with the present invention and the devices including these patterned films represent further aspects of the present invention.

20 The patterned film prepared in accordance with any one of the processes of the present invention and devices, materials coated with or including these multilayer films represent further aspects of the present invention.

As is evident from the above description the invention allows the preparation of a large  
25 variety of patterned films and structures. The processes of the present invention and the patterned structures formed may have use in the following applications:

- 1) electron emitters
- 2) field-emission transistors
- 30 3) photovoltaic cells and light emitting diodes with region-specific characteristics, and electrodes therefore

- 8 -

- 4) optoelectronic elements
- 5) bismuth actuators
- 7) chemical and biological sensors with region-specific characteristics
- 8) gas storages
- 5 9) molecular-filtration membranes
- 10) region-specific energy absorbing materials
- 11) flexible optoelectronic devices.

The invention will now be described with reference to the following examples and drawings  
10 which illustrate some preferred embodiments of the invention. However it should be understood that the particularity of the following description is not to supersede the generality of the invention previously described.

Referring to the drawings:

15

Figure 1 is a diagrammatic representation of a pyrolysis flow reactor suitable for preparing aligned carbon nanotubes.

Figure 2a is a schematic diagram showing the stages involved in the preparation of a patterned  
20 layer of aligned carbon nanotubes according to a micro-contact printing process.

Figure 2b is a schematic diagram showing the stages involved in the preparation of a patterned layer of aligned carbon nanotubes according to a micro-molding technique.

25 Figure 3a is a scanning electron microscopic image of patterned octadecylsiloxane self assembling monolayers on quartz glass plates. The black and white lines represent SiO<sub>2</sub> and SAM respectively.

Figure 3b is a scanning electron microscopic image of a pattern of DNQ-novolac photoresist  
30 selectively adsorbed in the OTS-free regions of the plate of Figure 2A.

- 9 -

Figure 3c is a scanning electron microscopic image of carbon-surrounded Fe particles selectively diffused in the polymer-free regions.

Figure 3d is an EDX profile of C and Fe. The scanning path for the EDS analysers is  
5 indicated by the line between points A and B.

Figure 3e is a scanning electron microscopic image of a pattern of aligned carbon nanotubes prepared using a micro-contact printing technique.

10 Figure 3f is a high magnification image of the aligned carbon nanotube pattern of Figure 3e.

Figure 4a is an optional microscopic image of the patterned surface of a PDMS mold.

Figure 4b is a scanning electron microscope image of the DNQ-novolac photoresist pattern  
15 preparing using a micro-molding technique with the stamp of Figure 3a.

Figure 4c is a scanning electron microscopic image of aligned carbon nanotube patterns prepared from the prepatterned substrate of Figure 4b.

20 Figure 4d is a higher magnification image of the pattern shown in Figure 4c.

## EXAMPLES

### 25 Example 1

Quartz glass plates were cleaned by heating in a Piranha solution (a mixture of 98%  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$  at 7:3 v/v) at 70°C for *ca.* 30 min, followed by thoroughly rinsing with deionized water. PDMS stamp was used for patterning an octadecyltrichlorosiloxane (OST) SAM layer on the cleaned quartz surface. After the contact transfer of the "ink" (i.e. 0.2%  
30 w/w of OST in hexane), the PDMS stamp was left in contact with the substrate for 15-30

- 10 -

seconds, and the patterned substrate was then immersed into a diazonaphthoquinone (DNQ)-modified cresol novolak photoresist solution (0.5 ~ 1.0 mg/ml) in ethoxyethyl acetate/acetone (1/10 ~ 1/5 v/v) for *ca.* 1s for selective absorption of the polymer into the OST-free regions. The polymer prepatterned quartz plate was heated at high temperature under Ar atmosphere  
5 to carbonize the photoresist polymer into a carbon layer. The carbonization was carried out by heating the patterned DNQ-novolac photoresist coating at 150°C, 300°C, 500°C, 700°C and 900°C for 30 minutes at each temperature. Carbonization of certain polymers has previously been reported (see, for example: (a) Kyotani, T.; Nagai, T.; Inoue, S.; Tomita, A. *Chem. Mater.* **1997**, 9, 609. (b) Parthasarathy, R.V.; Phani, K.L.N.; Marin, C.R. *Adv.*  
10 *Mater.* **1995**, 7, 896). The carbon nanotube patterns were then prepared by selectively growing aligned nanotubes in the photoresist-free regions by pyrolysis of FePc under Ar/H<sub>2</sub> at 800-1000°C.

Figures 2a & b represent typical scanning electron microscopic (SEM, XL-30 FEG SEM,  
15 Philips) images of patterned octadecylsiloxane SAMs on quartz glass plates and patterns of DNQ-novolac photoresist selectively-absorbed in the OTS-free regions. As can be seen, the patterned structures shown in Figures 2a & b are perfectly matched to each other with the photoresist lines interdispersed between the OTS lines in Figure 2b. Upon heating the prepatterned quartz plate associated with Figure 2b at high temperatures under Ar atmosphere,  
20 the DNQ-novolac photoresist layer was found to be carbonized into carbon black and remained on the quartz substrate while OTS molecules decomposed away from the surface. Carbonization of the photoresist polymer was, most probably, due to the crosslinking effect of sulfate species originated from the decomposition of *o*-diazonaphoquinone groups, as the X-ray photoelectron spectroscopic (XPS, Kratos Analytical, monochromatized Al K $\alpha$  at  
25 200W) and energy dispersive X-ray (EDX) analyses on the carbonized layer indicated the presence of carbon with a trace amount of sulfate. Figure 2c, together with the associated EDX profiles of C and Fe given in Figure 2d, clearly shows that the carbon-surrounded Fe particles formed at the initial stage of the pyrolysis of FePc preferentially deposited in the regions uncovered by the carbonized polymer pattern, presumably caused by a localized  
30 surface energy effect associated with the prepatterned substrate. Further pyrolyzing FePc under Ar/H<sub>2</sub> at 800-1000°C, therefore, led to region-specific growth of aligned nanotubes in

the polymer-free regions as the presence of metal catalysts is known to be mandatory for the nucleation and growth of carbon nanotubes by pyrolysis of FePc. Figure 2e represents a typical SEM image for the aligned nanotube micropatterns thus prepared. The width of the aligned nanotube arrays in Figure 2e is seen to be *ca.* 0.8  $\mu\text{m}$ , which is almost the same value  
5 as that for OTS lines seen in Figures 2a & b. Inspection of Figure 2e at a higher magnification (Figure 2f) shows that the aligned nanotubes are densely packed along the line length, but only a few of the nanotubes were observed across the line width in some of the nanotube lines.

## 10 Example 2

A drop of the DNQ-novolak photoresist in the ethoxyethyl acetate/acetone (15 ~ 20 % w/w) was spread on a quartz plate, and PDMS stamp was then pressed on the polymer coated quartz surface. After having dried in an oven at 80 ~ 100°C for about 30 min, the PDMS stamp was  
15 removed leading to a polymer-patterned substrate. The polymer prepatterned quartz plate was heated at high temperature under Ar atmosphere to carbonize the photoresist polymer into a carbon layer. The carbon nanotube patterns were then prepared by selectively growing aligned nanotubes in the photoresist-free regions by pyrolysis of FePc under Ar/H<sub>2</sub> at 800-1000°C.

20

DNQ-novolak photoresist patterns were prepared by the solvent-assisted micro-molding (SAMIM) method illustrated in Figure 1b. The structure of the PDMS mold used in this study is shown in Figure 3a, while the corresponding SEM image of the resulting photoresist pattern is given in Figure 3b. Prior to the region-specific growth of aligned nanotubes by  
25 pyrolysis of FePc under Ar/H<sub>2</sub> at 800-1000°C, the polymer patterned quartz plate was carbonized at high temperatures under Ar atmosphere as is the case with the micro-contact printing approach. Figures 3c & d show typical SEM images for the aligned nanotube patterns thus prepared. Unlike the micro-contact printing patterning, however, the micro-molding technique eliminates the SAM pattern formation and selective adsorption of DNQ-  
30 novolak photoresist chains involved in the micro-contact printing method, and hence serves as a more convenient approach for fabricating micro-/nano-patterns of the aligned nanotubes.





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THE CLAIMS:

1. A process for preparing a patterned layer of aligned carbon nanotubes on a substrate including:

5 applying a pattern of polymeric material to the surface of a substrate capable of supporting nanotube growth using a soft-lithographic technique;

subjecting said polymeric material to carbonization to form a patterned layer of carbonized polymer on the surface of the substrate; or

10

synthesising a layer of aligned carbon nanotubes on regions of said substrate to which carbonised polymer is not attached to provide a patterned layer of aligned carbon nanotubes on said substrate.

15 2. A process according to claim 1 wherein the polymeric material is a photoresist or photoresponsive material.

3. The process according to claim 2 wherein the polymeric material is (DNQ)-modified cresol novolac resin or Ozatek PL 14 (from Hoechst).

20

4. A process according to claim 1 wherein the polymeric material is selected from the group consisting of epoxy resins, PEO, polyanilines, polymethyl methacrylate, polystyrenes, polydienes, and plasma polymers derived from saturated or unsaturated alcohols, ketones, aldehydes, amines or amides.

25

5. A process according to claim 1 where the substrate is a glass.

6. A process according to claim 1 wherein the substrate is selected from the group consisting of quartz glass, graphite, mica, mesoporous silica, silicon wafer, nanoporous  
30 alumina and ceramic plates.

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7. The process according to claim 6 wherein the substrate is quartz glass or silicon wafer.
8. The process according to claim 1 wherein the substrate comprises a coating of a material which is capable of supporting carbon nanotube growth under the conditions employed.  
5
9. The process according to claim 8 wherein the coating is selected from the group consisting of a metal, metal alloy or compound thereof having conducting or semiconducting properties.  
10
10. The process according to claim 9 wherein the coating is a metal selected from the group consisting of Au, Pt, Cu, Cr, Ni, Fe, Co and Pd.
11. The process according to claim 9 wherein the coating is a metal compound or metal alloy compound selected from an oxide, a carbide, a nitride, a sulfide or a boride.  
15
12. The process according to claim 11 wherein the coating is a metal oxide selected from the group consisting of indium tin oxide (ITO),  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{MgO}$ .
- 20 13. The process according to claim 9 wherein the coating is a semiconducting material selected from the group consisting of gallium arsenide, aluminium arsenide, aluminium sulphide and gallium sulphide.
14. A process according to claim 1 wherein the soft lithographic technique is a microcontact printing technique.  
25
15. A process according to claim 14 wherein self-assembling monolayers (SAMS) of a molecular ink is applied to the surface of said substrate in a region specific manner, followed by adsorption of said polymeric material in the SAM-free regions).  
30
16. A process according to claim 15 wherein the molecular ink is an alkylsiloxane.

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17. A process according to claim 15 wherein the molecular ink is applied using a stamp.
18. A process according to claim 14 wherein the hydrophobicity and hydrophilicity of the surface of said substrate is altered by the region specific transfer to the surface of the substrate  
5 of a material which alters the hydrophobicity or hydrophilicity of the surface, followed by the adsorption of the polymer in the more hydrophobic regions of the substrate surface.
19. A process according to claim 1 wherein the soft lithographic technique is a micromolding technique.  
10
20. A process according to claim 19 wherein the micromolding technique comprises applying a thin layer of a solution of said polymeric material in a solvent to said substrate surface, sandwiching the solution between said substrate surface and a mold surface, said mold having incised areas corresponding to the pattern to be formed on the substrate surface,  
15 allowing the solvent to evaporate and removing the mold to provide a pattern of polymeric material on the substrate surface.
21. A process according to claim 20 wherein the mold is composed of PDMS, fluorocarbon or other solvent resistant elastomers.  
20
22. A process according to claim 1 wherein the polymeric material is carbonized by heating to a temperature at or above a temperature at which said polymeric material decomposes.
23. The process according to claim 1 wherein the aligned carbon nanotubes are synthesised  
25 by pyrolysis of a carbon-containing material in the presence of a suitable catalyst for nanotube formation.
24. The process according to claim 23 wherein the carbon-containing material is selected  
30 from alkanes, alkenes, alkynes or aromatic hydrocarbons and their derivatives, organometallic compounds of transition metals and other suitable evaporable metal complexes.

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25. The process according to claim 24 wherein the carbon-containing material is selected from methane, acetylene and benzene.

26. The process according to claim 24 wherein the organometallic compound is a  
5 transition metal phthalocyanine.

27. The process according to claim 24 wherein the organometallic compound is a metallocene.

10 28. The process according to claim 23 wherein the catalyst is a transition metal.

29. The process according to claim 28 wherein the transition metal is selected from the group consisting of Fe, Co, Al, Ni, Mn, Pd, Cr or alloys thereof in any suitable oxidation state.

15

30. The process according to claim 23 wherein the catalyst is incorporated in the carbon-containing material.

31. The process according to claim 30 wherein the catalyst is selected from the group  
20 consisting of Fe(II) phthalocyanine, Ni(II) phthalocyanine and ferrocene.

32. The process according to claim 30 further comprising an additional source of catalyst.

33. The process according to claim 30 further comprising an additional source of carbon-  
25 containing material.

34. The process according to claim 23 wherein the pyrolysis is carried out at 500°C to 1100°C.

30 35. The process according to claim 1 wherein the process comprises the further step of dissociating the aligned carbon nanotubes from the substrate.

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36. The process according to claim 35 wherein the substrate is quartz glass and dissociation is effected by immersing the sample in an aqueous hydrofluoric acid solution (10-40% w/w).

5 37. The process according to claim 35 wherein dissociation comprises transferring the patterned carbon nanotube layer to another substrate.

38. The process according to claim 37 wherein the other substrate is elected from the group consisting of another substrate capable of supporting carbon nanotube growth, a metal,  
10 metal oxide, semi-conductor material or a polymer.

39. The process according to claim 38 wherein the polymer is selected from the group consisting of adhesive coated polymers, conjugated (conducting)polymers, temperature/pressure responsive polymers, bioactive polymers and engineering resins.

15

40. The process according to claim 39 wherein the adhesive coated polymer is cellulose.

41. A patterned carbon nanotube film prepared in accordance with claim 1.

20 42. A device comprising a patterned carbon nanotube film prepared in accordance with claim 1.

43. A photovoltaic cell comprising a patterned carbon nanotube film prepared in accordance with claim 1.

25

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number  
WO 01/21863 A1

(51) International Patent Classification<sup>7</sup>: C30B 29/66,  
29/02, 23/04, C01B 31/02

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(21) International Application Number: PCT/AU00/01180

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(22) International Filing Date:  
22 September 2000 (22.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
PQ 3041 23 September 1999 (23.09.1999) AU

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AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,  
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,  
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,  
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,  
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,  
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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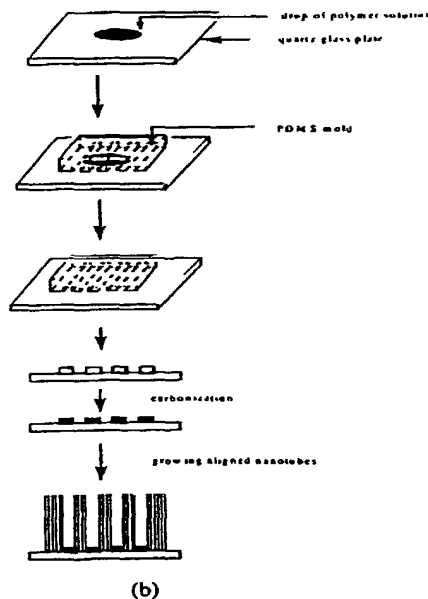
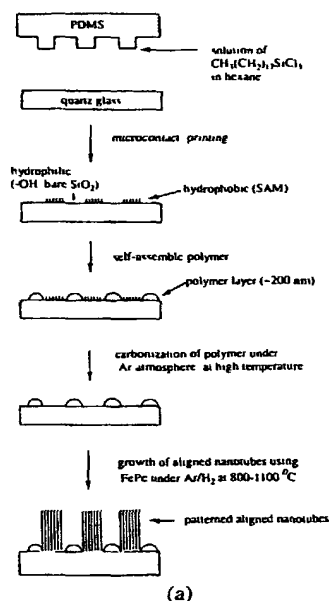
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Published:

— With international search report.

[Continued on next page]

(54) Title: PATTERNED CARBON NANOTUBES



(57) Abstract: A process for preparing a patterned layer of aligned carbon nanotubes on a substrate including: applying a pattern of polymeric material to the surface of a substrate capable of supporting nanotube growth using a soft-lithographic technique; subjecting said polymeric material to carbonization to form a patterned layer of carbonized polymer on the surface of the substrate; synthesising a layer of aligned carbon nanotubes on regions of said substrate to which carbonized polymer is not attached to provide a patterned layer of aligned carbon nanotubes on said substrate.

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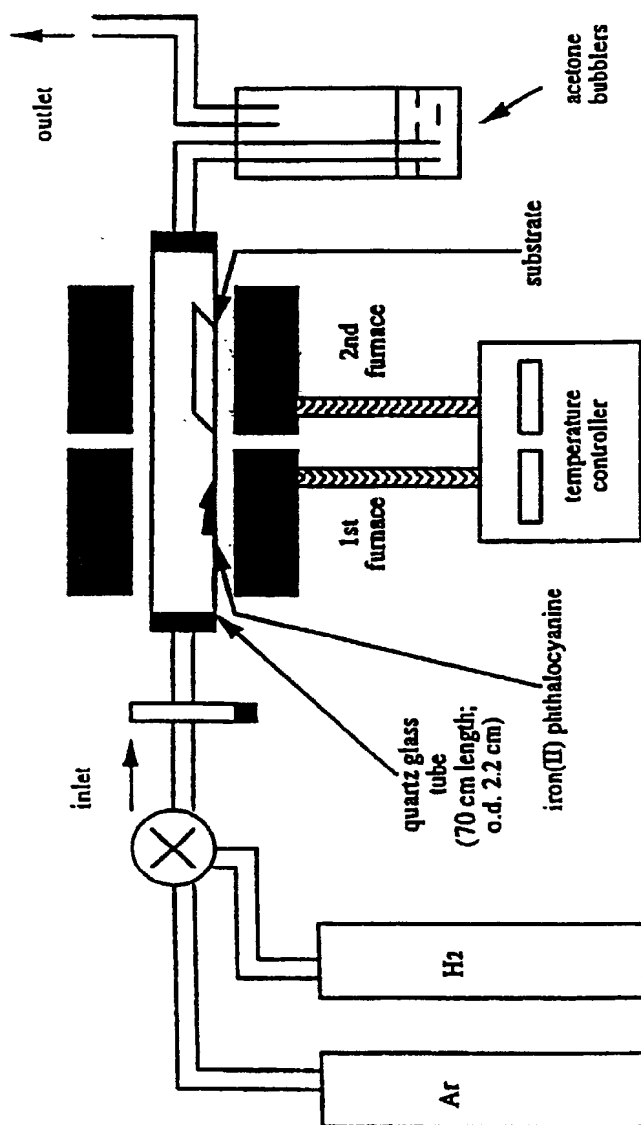


FIGURE 1

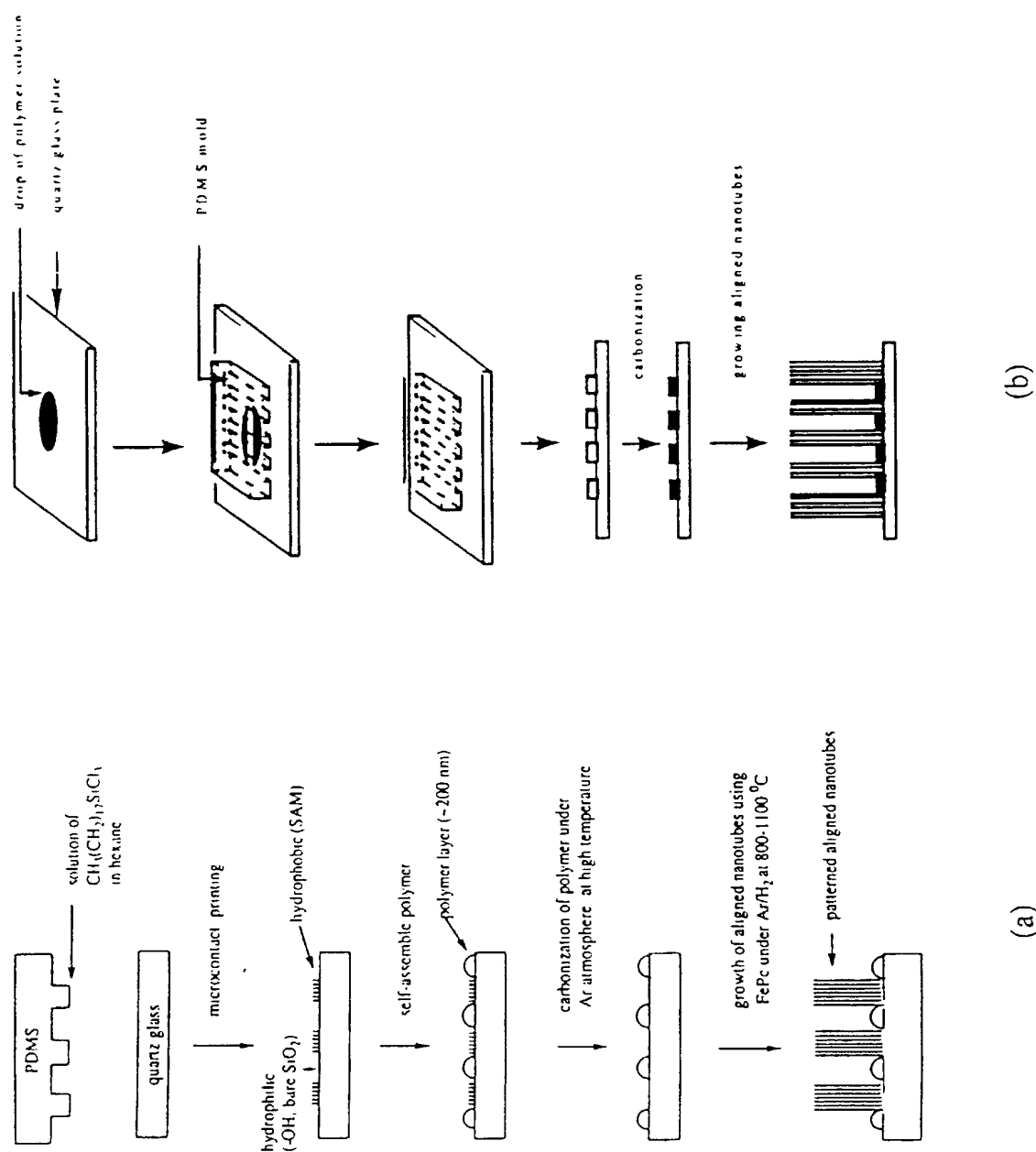


FIGURE 2

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Figure 3(a)

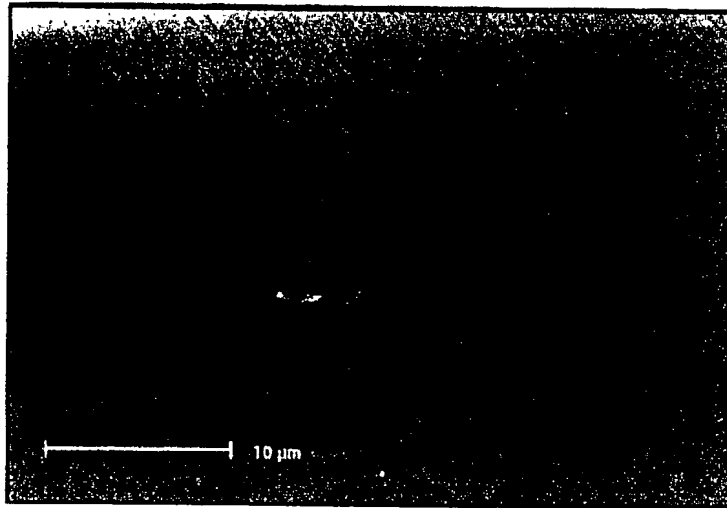


Figure 3(b)

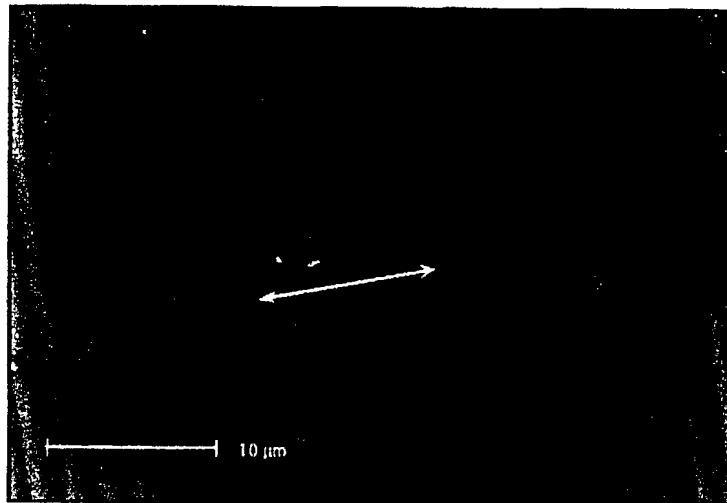
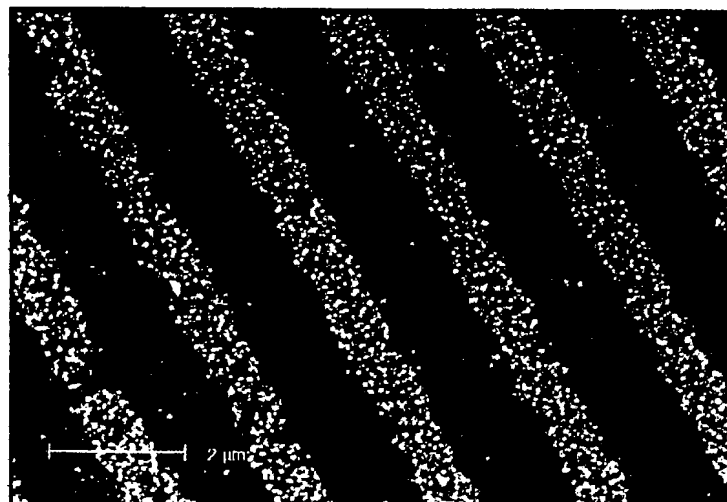


Figure 3(c)



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Figure 3(d)

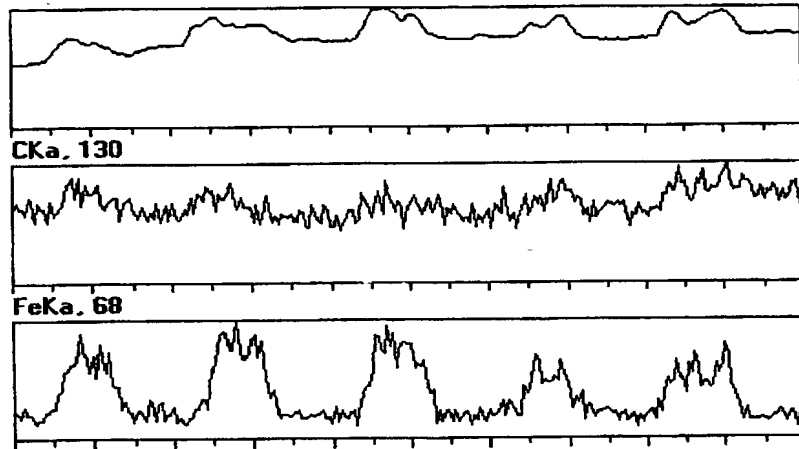


Figure 3(e)

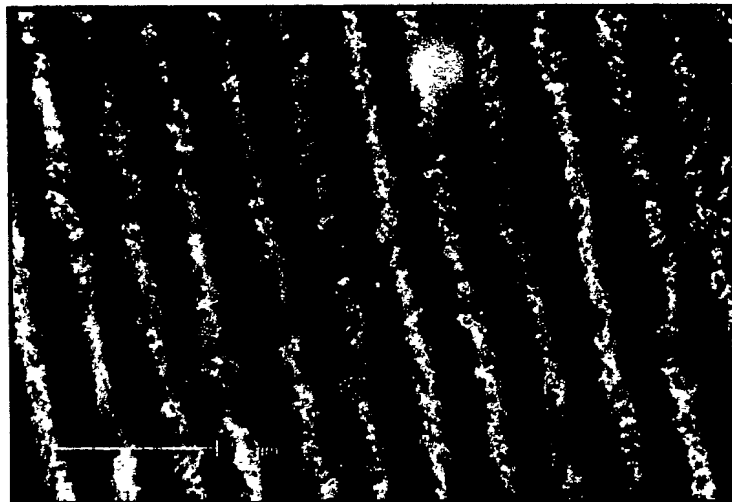


Figure 3(f)

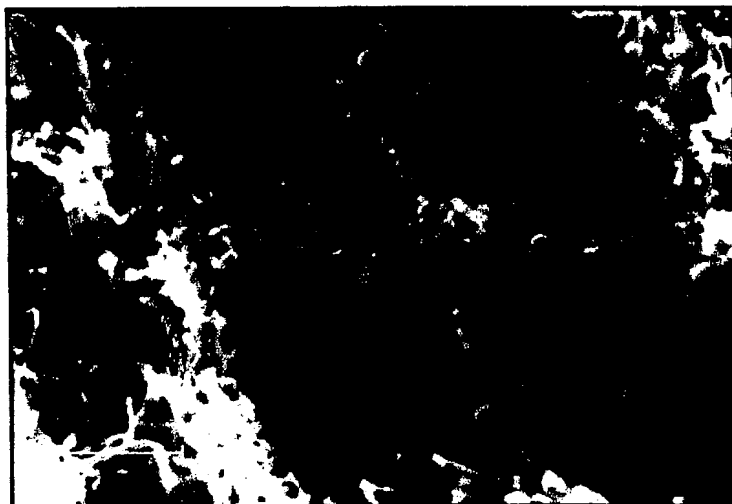


Figure 4(a)

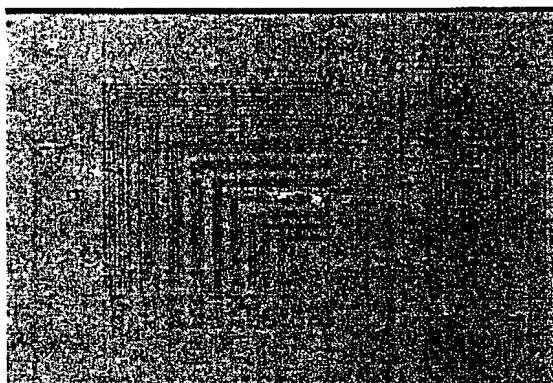


Figure 4(b)

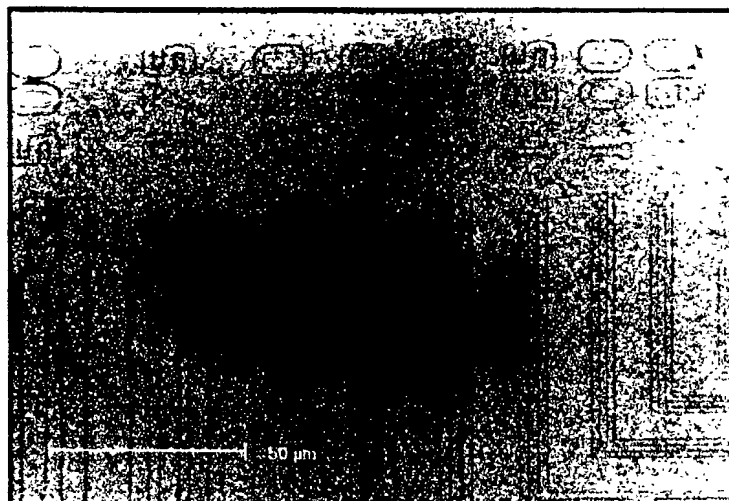


Figure 4(c)

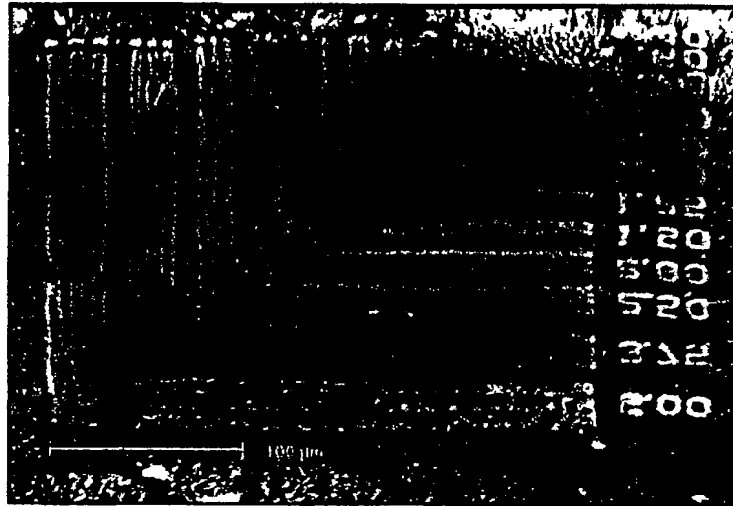
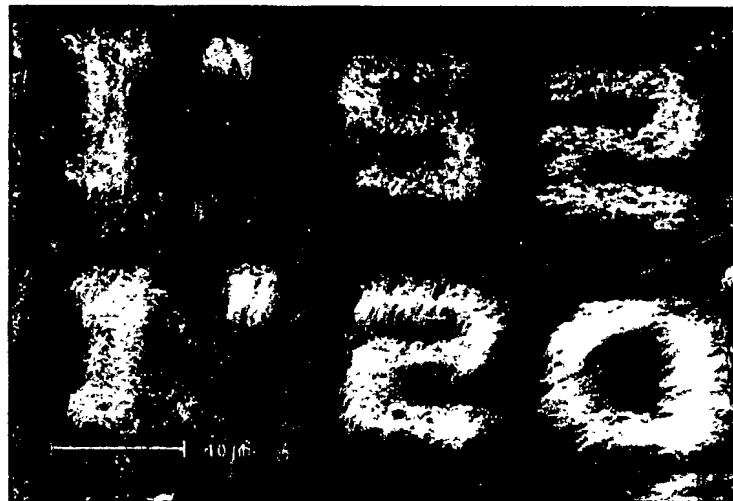


Figure 4(d)



**DECLARATION AND POWER OF ATTORNEY FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)**

As a below named inventor, I hereby declare that: My residence, mailing address, and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**Patterned carbon nanotubes** ✓

the application of which  
☐ is attached hereto

OR

☒ was filed on **22 September 2000** as United States Application Number or PCT International Application Number **PCT/AU00/01180** ✓ (Confirmation No. \_\_\_\_\_), and was amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified application, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part application(s), material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application(s) which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application(s) having a filing date before that of the application on which priority is claimed.

| Prior Foreign Application Number(s) | Country            | Foreign Filing Date        | Priority Claimed                    |                          |
|-------------------------------------|--------------------|----------------------------|-------------------------------------|--------------------------|
|                                     |                    |                            | Yes                                 | No                       |
| <b>PQ3041/99</b> ✓                  | <b>Australia</b> ✓ | <b>23 September 1999</b> ✓ | <input checked="" type="checkbox"/> | <input type="checkbox"/> |

I hereby claim domestic priority benefits under 35 United States Code §120 of any United States application(s), §119(e) of any United States provisional application(s), or §365(c) of any PCT International application(s) designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in a listed prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge my duty to disclose any information material to the patentability of this application as defined in 37 C.F.R. 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

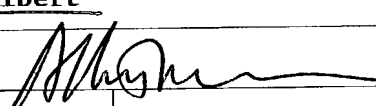
| Prior U.S. or International Application Number(s) | U.S. or International Filing Date | Status |
|---|-----------------------------------|--------|
| <b>PCT/AU00/01180</b> ✓                           | <b>22 September 2000</b> ✓        |        |

I hereby appoint all attorneys of **SUGHRUE MION, PLLC** who are listed under the USPTO Customer Number shown below as my attorneys to prosecute this application and to transact all business in the United States Patent and Trademark Office connected therewith, recognizing that the specific attorneys listed under that Customer Number may be changed from time to time at the sole discretion of Sughrue Mion, PLLC, and request that all correspondence about the application be addressed to the address filed under the same USPTO Customer Number.

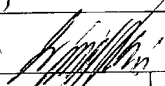


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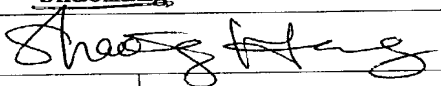
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